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On the entropy of solid and liquid metals

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With 7 figures in the text

The traditional use of the heat capacity at constant volume, C_V, in the theory of the solid state is based on the hypothesis that the changes of state when temperature and pressure are varied in such a way, that the volume is kept constant, should represent a particularly simple case. Attempts to survey our collected experimental knowledge in this field convinced the present writer that there is no real experimental support for this assumption and inspired the attempt to look for some better division of the observed heat capacity C_p than the division into C_V and $C_p - C_V$. After trials in other directions [1, 2], it was found that a theoretically natural division of the observed C_p values into a kinetic and a potential part led to the simple relationships reported in four recent papers [3, 4, 5, 6], concerning compressibility, potential energy, thermal expansion, diffusion and temperature dependence of resistivity. In certain simple cases these relationships also include the liquid state.

In the present paper the connections between the potential part of the entropy and the changes of volume will be discussed from the same point of view. The available data are for pressures of the order one atmosphere, which restricts us to the case of constant, practically zero, pressure.

Assuming zero pressure, the total entropy per mole is obtained, for a solid metal at T°K from

$$S = \int_0^T \frac{C}{T}\, dT, \tag{1}$$

where C is the heat capacity per mole at low pressure, and for a liquid metal from

$$S = \int_0^{T_f} \frac{C}{T}\, dT + \frac{Q_f}{T_f} + \int_{T_f}^{T} \frac{C}{T}\, dT, \tag{2}$$

where T_f is the absolute temperature of fusion and Q_f the total heat of fusion. On the same assumption as used in earlier papers, namely that the kinetic part of the molar heat capacity is approximately described by a Debye function increasing from zero at 0°K to $3R/2$ at high temperature, the kinetic part of the entropy at T°K thus is

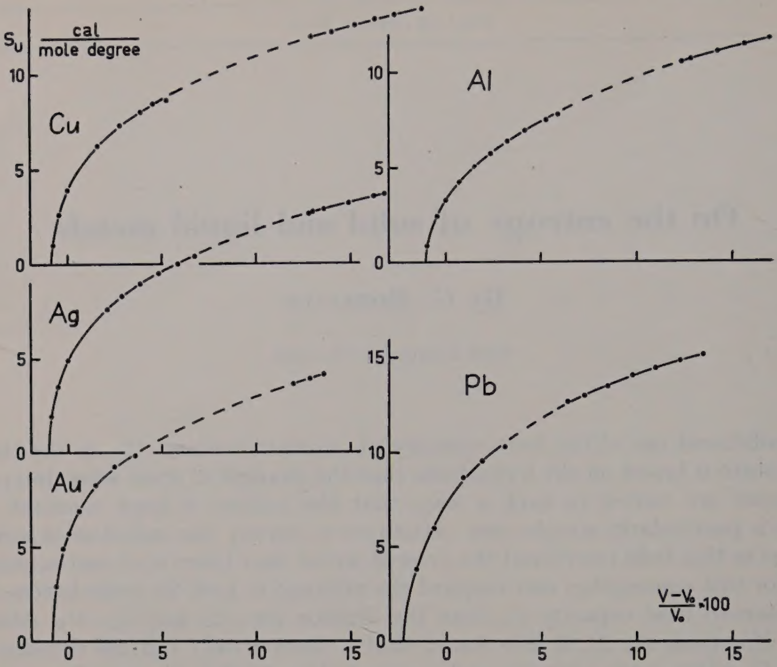

Fig. 1. Potential part of entropy versus thermal change of volume for face-centered cubic metals.

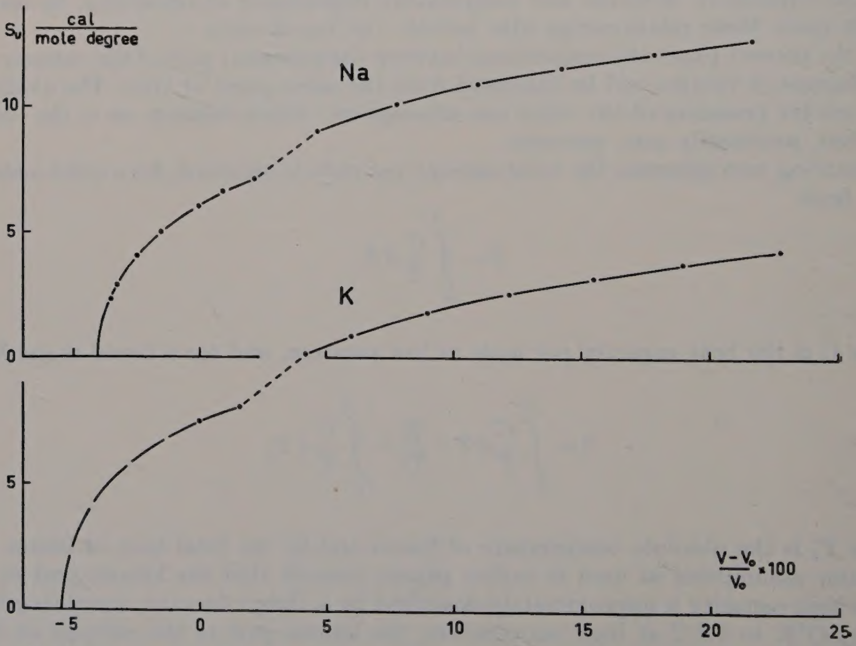

Fig. 2. Potential part of entropy versus thermal change of volume Na and K.

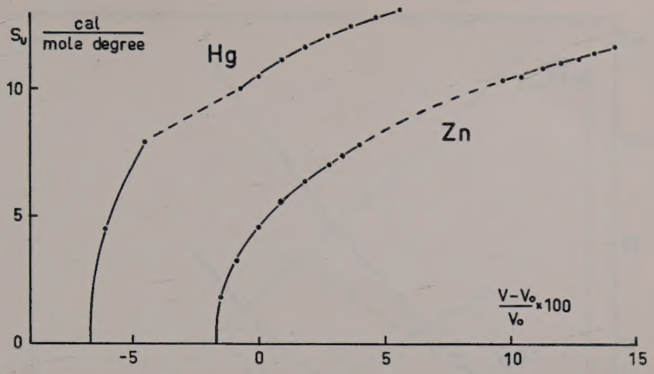

Fig. 3. Potential part of entropy versus thermal change of volume for Zn and Hg.

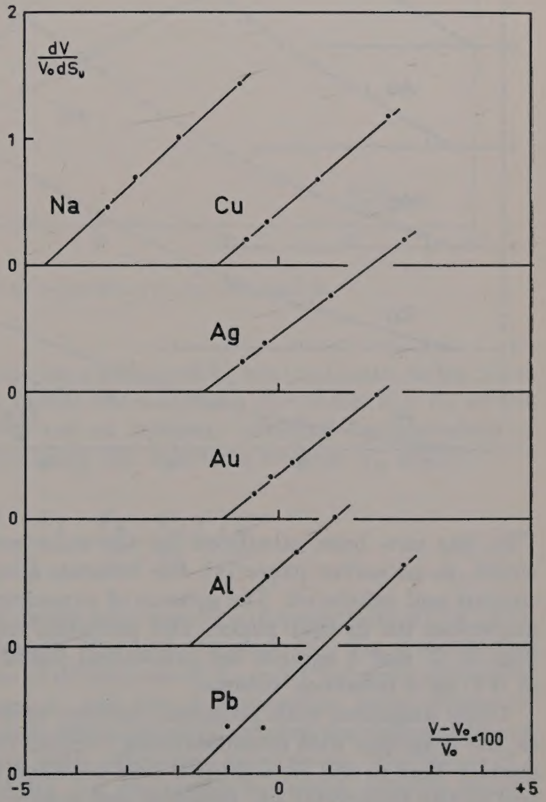

Fig. 4. Plots for the determination of constant c in equation (6).

$$S_K = \frac{3}{2} R D\left(\frac{T}{\theta}\right), \qquad (3)$$

where R is the gas constant, θ is the Debye temperature and $D(T/\theta)$ is the Debye function for entropy increasing from 0 to 1. The potential part of the entropy is the difference

$$S_U = S - S_K. \qquad (4)$$

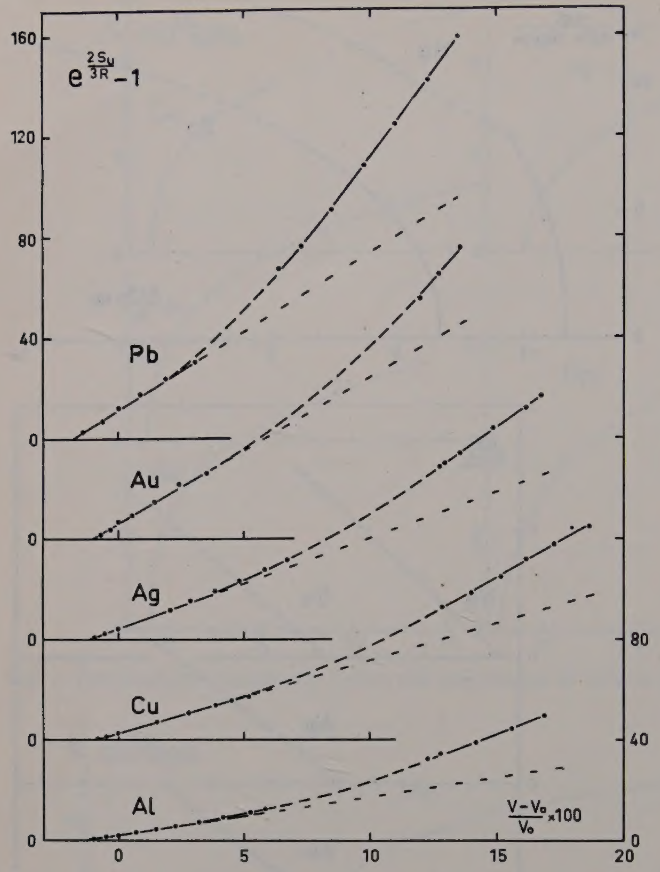

Fig. 5. Plots for illustrating equation (7) and for the determination of V_z for face-centered cubic metals.

S_U has now been calculated for the same metals and the same temperatures for which, in an earlier paper [4], the volumes and the potential energies had been calculated and tabulated. The sources of experimental data are also the same as those accounted for in that paper. The potential entropies thus obtained are plotted in Figs. 1, 2, and 3 against the procentual volume changes with the mole volume V_0 at 0°C as a reference volume.

These diagrams with potential entropy versus volume give the same impression as the diagrams with potential energy versus volume given in the previous paper [4], namely that in the close-packed face-centered cubic metals Cu, Ag, Au, Al, and Pb and in the hexagonal Zn, fusion is just a part of a transformation beginning in the solid and continuing in the liquid state, while in the body-centered cubic Na and K, and in Hg, fusion also means a structural change.

The search of a formula to describe the potential entropy as a function of volume led to an expression of the form

$$S_U = c \ln \frac{V - V_a + V_z}{V_z}, \tag{5}$$

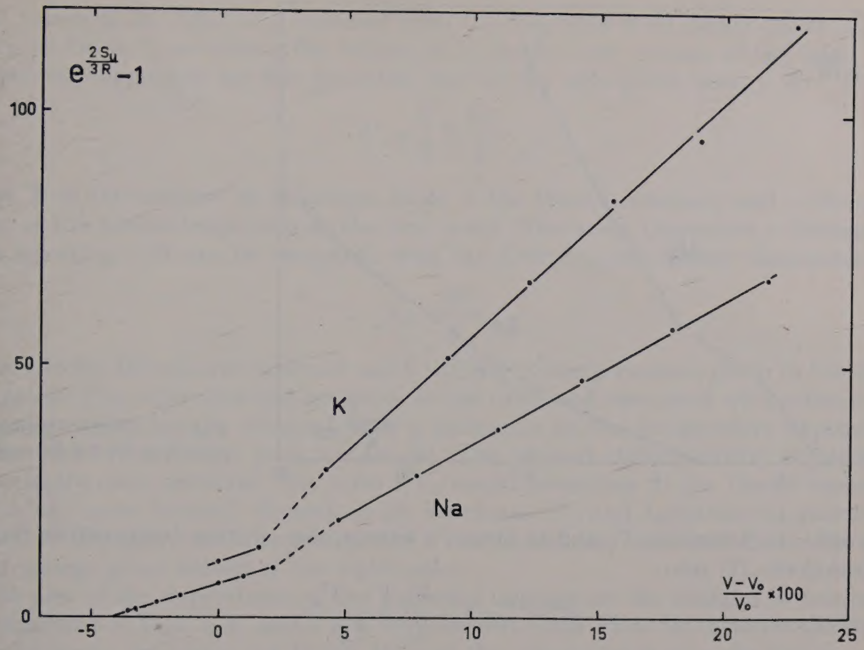

Fig. 6. Plots illustrating equation (7) for Na and K.

where V_a is the mole volume at absolute zero and c and V_z are constants, to be determined experimentally. The formula fulfills the condition $S=O$ for $V=V_a$ at the zero point. In order to determine c we use an equation obtained by derivation of (5) and a simple transformation introducing the reference volume V_0 at 0°C

$$\frac{1}{V_0}\frac{dV}{dS_U}=\frac{1}{c}\,\frac{V-V_0}{V_0}+\frac{V_0-V_a+V_z}{V_z}. \tag{6}$$

If equation (6) is valid with constant values for c and V_z a diagram with $dV/V_0\,dS_U$ against $(V-V_0)/V_0$ should give a straight line with the slope $1/c$. Fig. 4 shows diagrams of this type obtained by the use of differences of S_U and V between successive points in the diagrams of Figs. 1 and 2, and the corresponding mean values of $(V-V_0)/V_0$. For temperatures far enough below the melting point the values obtained arrange themselves along straight lines with nearly the same slopes. The values of c obtained for Cu, Ag, Au, Al, Pb, and Na, i.e. the metals for which suitable experimental results are available, are in order 2.93, 3.33, 3.14, 2.95, 2.60, 2.93, and give as a mean value $c=2.98\pm 0.10$ cal/mole degree which agrees with the value $3R/2=2.98$ cal/mole degree. This result could also have been predicted from theoretical considerations. Thus we have for the range of temperature well below the melting points

$$S_U=\frac{3R}{2}\ln\frac{V-V_a+V_z}{V_z}. \tag{7}$$

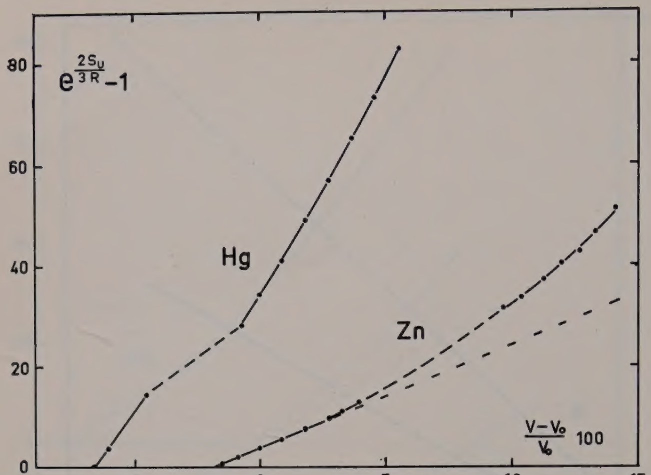

Fig. 7. Plots illustrating equation (7) for Zn and Hg.

In order to determine V_z and to obtain a survey also of other temperature ranges, we transform (7) into

$$e^{2S_U/3R}-1=\frac{V_0}{V_z}\,\frac{V-V_0}{V_0}. \tag{8}$$

Plots of the left side of this equation versus $(V-V_0)/V_0$ in Figs. 5, 6, and 7 give in the range of temperatures below and not too near the melting points straight lines from the slopes of which we have determined the values for V_z/V_0 given in Table 1.

These values allow an interesting interpretation of V_z as a change in volume due to the zero-point energy. If we assume that the ratio of the zero-point volume V_z and the potential half of the zero-point energy U_z is the same as the ratio at $T=O$ of thermal change in volume ΔV and thermal change in potential energy ΔU, we have

$$U_z=\frac{\Delta U}{\Delta V}V_z=\frac{\Delta U}{\frac{\Delta V}{V_0}}\,\frac{V_z}{V_0}. \tag{9}$$

Table 1. Calculated mean frequency $\bar{\nu}$ compared with the Debye frequency ν_D.

	$\frac{V_z}{V_0}\times 100$	$\frac{\Delta U}{\frac{\Delta V}{V_0}\times 100}$ $\frac{\text{cal}}{\text{mole}}$	U_z $\frac{\text{cal}}{\text{mole}}$	θ	$\frac{\bar{\nu}}{\nu_D}$	
					from entropy	from resistivity
Al	0.613	455	279	398	0.47	0.66
Cu	0.355	628	223	325	0.46	0.58
Ag	0.266	658	175	215	0.55	0.59
Au	0.160	788	126	190	0.45	0.60
Pb	0.170	346	59	88	0.45	0.57
Na	0.626	186	116	159	0.49	0.80

With values of $\Delta U/(\Delta V/V_0)$ obtained from the diagrams in an earlier paper [4] and shown in Table 1, we obtain the values of U_z in the next column of the table. The theoretical expression for the potential half of the zero-point energy is

$$U_z = \frac{3}{2} N \frac{h\bar{\nu}}{2}, \tag{10}$$

where N is the number of atoms pro mole, h the Planck constant, and $\bar{\nu}$ the mean value of the lattice frequences at the zero point. The mean frequences ν determined from equation (10) can be compared with the Debye characteristic frequences

$$\nu_D = \frac{k\theta}{h}, \tag{11}$$

where k is the Boltzmann constant and θ the Debye temperatures, given in the table. The ratios $\bar{\nu}/\nu_D$ thus obtained are given in the table and compared with ratios in the last column which were obtained from a discussion on the temperature dependence of the resistivity in the pure metals [6]. The present determination is probably numerically more accurate. The ratio ν/ν_D would according to the Debye theory be 0.75 while more detailed discussions by Blackman [7] and Leighton [8] give lower values. In any case, our interpretation of V_z as an increase in volume due to the zero-point energy gives values of the right order.

The plot of the dependence of the potential entropy on the changes in volume in the diagrams of Figs. 5, 6, and 7 is a very sensitive one. Thus for instance the difference between the curve for liquid Pb and the extrapolated straight line means a maximum difference in entropy of only about ten per cent. There seems to be no doubt, however, that there is a general increase of the entropy in the liquid face-centered cubic metals and in liquid Zn above the values given by equation (7). It is possible that this increase is due to some sort of special lattice disturbances.

Whether the deviation from the straight lines representing equation (7) begins already in the solid state or not, cannot be judged from our diagrams which are based on tabulated values obtained as smoothed mean values from different experimental sources and which seem to be especially uncertain near below the melting point. This question, which is of considerable interest, necessitates more detailed studies of the experimental data in the range below the melting point and in many cases also new measurements.

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